

STUDIES IN SOL-GEL PROCESSING FROM A TITANIUM ALKOXIDE SOL

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by
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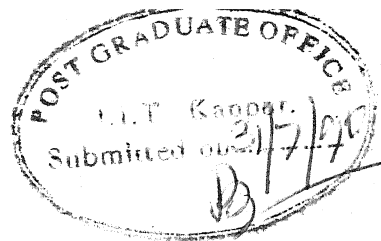
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my parents



CERTIFICATE

This is to certify that this work on "Studies in Sol-Gel processing from Titanium Alkoxide Sol" by Pranod Kumar Sharma has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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ABSTRACT

Sol-gel processing from a titanium tetra isobutoxide (TTIB) sol has been studied. Effects of DEA content, water content, catalyst and mechanical mixing routes on the stability of the sol have been investigated. It is determined that about 0.6 mol of DEA per mole of TTIB are needed to permit reasonable time for processing of clear gels. It has been possible to enhance the water content in the sol to more than 6.5 molar ratio by a combination of techniques such as refluxing, and ultrasonication.

Powders of PbO coated with a titania gel have been prepared. Temperature for the formation of lead titrate is found to be reduce by more than 110°C in then powders. The coating is found to be not very homogeneous. The weight loss on calcination, related to the amount of unhydrolyzed alkoxy groups can be reduced by using the techniques developed in this work.

CHAPTER 1

INTRODUCTION

I.1: The Sol-Gel Method for Ceramics and Glasses

The ceramic products obtained by the traditional methods [1,2,3] such as pressing, extrusion, slip casting are generally non-homogeneous, porous, impure and require a high firing temperature. To rectify these problems the ceramic and glass scientists have always looked for a new method for preparation of glass and ceramics.

In the last few years, the so called "Sol-Gel" methods have been receiving a great deal of scientific attention among the ceramic and glass scientist. To many, these sol-gel methods offer new approaches to the preparation of glasses and ceramics. The history [4] of "sol-gel" processes is not new. Bayer and Geffecken [5,6] found about 50 years ago that the oxide coatings deposited from solutions. About 20 years back Schroeder [7] developed a thin film from the same method for single oxide and mixed oxide layer. A lot of research work has been done in the field of "sol-gel" processes since 1971. It has been known since then, that any type of multicomponent oxide can be synthesized using the alkoxides of various elements by the sol-gel process.

I.2 : The "Sol-Gel" process :

In the sol-gel process [8] a "Sol" undergoes a

transformation to give rise to a "gel". All sol-gel processes start with a sol. A "Sol" can be defined as a suspension of submicron particles in suspension in a liquid. These particles can be fine powders or small molecules as in a sol of metallo-organic compounds in alcohol. A "Gel" can be defined as a rigid, porous mass derived from the transition of sol. Colloidal sols formed by the suspension of submicron particles in aqueous medium are called "Physical sols" and the processes with these solutions are called "Physical sol gel processes". In chemical sol-gel processes, the chemical reactions take place to give rise to an oxide network called "chemo sol" and processes is called "chemical sol-gel processes"[9,10].

I.3. Alkoxide Route for Sol-gel Processes

There are two important sol-gel processes [11] namely

1) Alkoxide Method explained by Johnson et.al. and K. Kamiya et.al. [12-16].

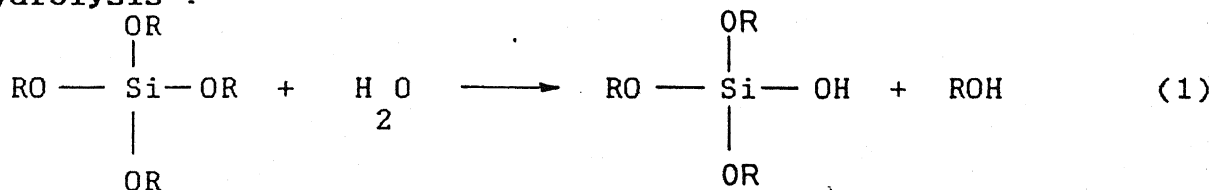
2) Colloidal Method explained by Robinowich, and Segal and Johnson [17,18].

Metal alkoxides are generally very reactive species which may be due to the presence of electronegative alkoxy groups which make metal atoms highly positively charged to attract the nucleophiles. One of the predominant characteristics of metal

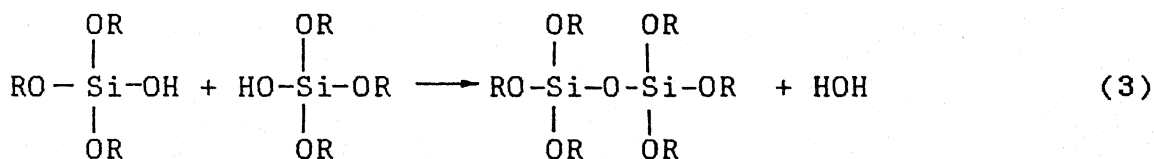
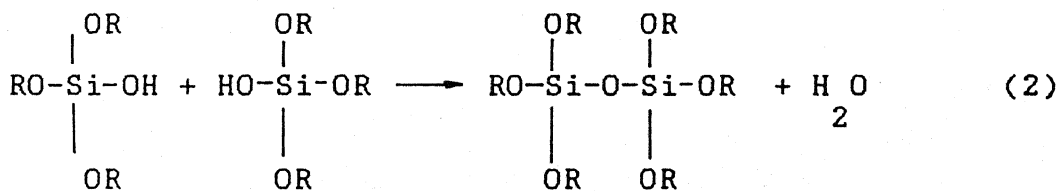
alkoxides is their extreme susceptibility to hydrolysis by atmospheric moisture and thus they require careful handling. In the sol gel process the metal alkoxide is taken as precursor for preparation of sol [19-20]. The metal alkoxides are hydrolyzable. Their subsequent condensation after hydrolysis gives rise to a gel method. When gel is heated to high temperature the entrapped solvents and water etc. are removed and an amorphous metal oxide forms.

The main reactions involved in the sol-gel process are given below taking the well studied silicon alkoxide (Tetra ethyl orthosilicate) $\text{Si}(\text{OC}_2\text{H}_5)_4$:

Hydrolysis :



Condensation starts before a molecule is fully hydrolysed. It can occur by two ways :



The reaction (1) is faster than (2) & (3) if there is no coordination polymerization involving either alkoxide oxygen or exo-oxygen or both and result in precipitation. However controlled hydrolysis will give soluble polymeric intermediate which undergo further polymerization to form a clear gel. As the water and alkoxide are immiscible, to carry out the reaction between these two, a common solvent is needed. Alcoholic medium is generally used. The mixture of alkoxide and alcohol solutions are added to the mixture containing alcohol and required amount of water.

I.4 Alkoxide Precursor :

In sol-gel processes the metal alkoxide are used as precursor for preparation of solution. The Chemical modification of alkoxide precursors are explained by Sanche et al [21]. The alkoxy in alkoxides are highly electronegative and make metal positively charged to attract the negative species as illustrated earlier. Their reaction is very active.

Boyd explained that among $\text{Ti}[\text{oPr}]_4$ and $\text{Ti}[\text{oBu}]_4$, the $\text{Ti}[\text{oPr}]_4$ is more sensitive towards moisture. So $\text{Ti}[\text{oBu}]_4$ is easier to handle as alkoxy precursor to get longer life of sol. But $\text{Ti}[\text{oBu}]_4$ is also very reactive as compared to other metal alkoxide so an external reagent is needed to suppress the

alkoxide so an external reagent is needed to suppress the hydrolysis and precipitation of oxides. Ethyl glycol, diethanolamine [DEA] and diethyl glycol etc. are generally used for this purpose as explained by Yasutaka [22].

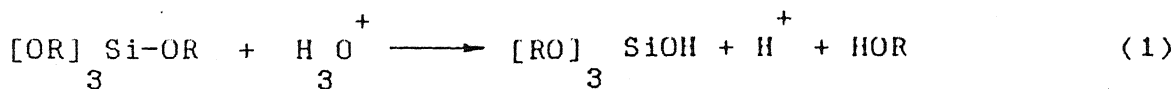
I.5 - Catalyst :

The gelation process of metal alkoxides involves both hydrolysis and polymerization reactions. The effects of catalysts in both of these reactions is complex, depending not only on the pH, but also upon the reaction mechanisms of each catalytic agent [23].

I.5.a : Acid Catalysed Hydrolysis :

Yoshihiro et al [24] stated that the acid retards the polymerization reaction, suppressing rapid gelation and also preventing the formation of polymer network. Thus on increasing the amount of acid, fresh gel changed from transparent to opaque and then to powder like. Also shrinkage rate increased with increased amount of acid. Direct TEM observations determined that acid catalyzed gels were fibrous in character and homogeneous. Analyzed by EDX and SAD analysis indicated that acidic gels were chemically homogeneous and microcrystalline.

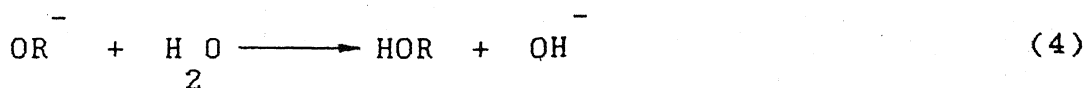
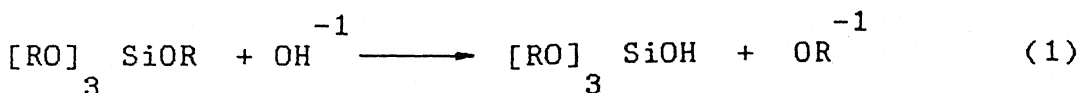
The acid catalyzed hydrolysis is an electrophilic
? reaction that can be expressed by following equation :



In this kind of hydrolysis reaction, the reaction rate is governed by the concentration of hydronium ions in solution [17,25-28].

I.5.b : Base Catalysed hydrolysis :

The gels from base catalyzed solutions were translucent or cloudy with phase separation [26]. Also the TEM observations illustrated that base-catalyzed gels had a coarse texture, and are heterogeneous. In the base catalyzed hydrolysis, a nucleophilic substitution of hydroxyl ions for OR groups occurs. This reaction is presented by following equations :



Analogous to the acidic reaction, the rate of base catalyzed hydrolysis is a function of hydroxyl concentration in solution [29].

I.6: Factors affecting the sol-gel reaction paths :

Due to tremendous number of parameters numerous reaction paths are existing. The main influencing parameters are

1: Precursors :

e.g. : salts
 oxides
 alkoxides
 colloids

2: Reaction Conditions :

1. Reaction mode
2. Solvents
3. Temperature
4. Catalysts and pH
5. Amount of water

3: Mechanical parameters :

1. Stirring
2. Ultrasonic treatments
3. Refluxing

I.6.1 Precursor

Molecular precursors [30] require an activation reaction be transformed into species ready to perform a condensation reaction. In most of the cases this is a hydrolysis reaction.

As general rules, one can say the hydrolysis rate increases with

- increasing polarity on the Me-X bond.
- increasing the concentration of catalysts.
e.g. - Acid and Base
- with temperature.
- decreasing stabilization of the solvation or complex forming effect of solvents or complex formers.

It decreases, especially if alkoxides are used with

- increasing chain length of the alkyl chain.
- use of complex former.
e.g. - B-diketonate complex of Ti alkoxides.

I.6.2 Reaction Conditions :

The reaction mechanism [31] of sol-gel processes is affected by solvent, temperature, catalyst and pH.

I.6.2.1:Solvents :

It is presently assumed that for most gel systems the use of a solvent is desirable. The most common solvents used are the alcohols and most alcohols have relatively high vapour pressures, even at room temperature. The time of gelation can vary from few hours to days . In the loss of solvent through evaporation can be very appreciable one has the choice of a

closed system, an open system, or partially open system during gelation. Frequently, these aspects of the process is not quantitatively controlled. A cursory consideration would suggest that the amount of solvent lost during gelation must have significant influence on bulk density of gel and hence its porosity and probably the average size of the pores. Because the pores are related to the cracking of the gel as explained by Mackenzic [32], solvent losses must be one of the most important factors for conversion of liquid solution (solid suspension) to porous amorphous gel and this gel to less porous amorphous gel. So the pronounced affects due to solvent differences on the viscosity, surface tension of sol, difference in the bulk density of the gel after firing and also the specific surface area of the gel.

Further more the amount of solvent used can be influenced the gelation time as well as the microstructure of the gel since the concentration of the reactants in the solution gets altered.

I.6.2.2 Temperature :

Yamane and Okana [33] observed the effects of temperature on gelation of SiO_2 gels at from 54 to 70 C in an open system. The bulk densities of the gels were found to decrease from 1.46 gm/cm³ to 0.98 gm/cm³ at these two

temperatures respectively. The gelation times become shorter as the sol-gel reaction temperature becomes higher, because the reaction rate increases. It has been shown by Colby et al [34] that the following Arrhenius relationship is obeyed. The activation energy of about 10 K Cal/mol has been obtained for the gelation of silicon alkoxide solutions by both Colby et al [34] & Kinouchi et al [35]

$$\frac{1}{t_g} = A \exp. \left[- \frac{E^*}{RT} \right]$$

where

t_g = Gelation time
 E^* = Activation energy
 T = Temperature
 A & R = Constants

I.6.2.3: Reaction Model :

Open or Closed System :

The gelation time is much smaller for silicon alkoxide solution reached in the open container than for that reacted in the closed system observed by KOZUKA et al [36]. There are three possible reasons for this. In the open system, the vaporization

of reaction products such as alcohol and water, may promote the reactions. The incorporation of moisture from the air may promote the reactions towards polymerization, vaporization of solvents also increases the conc. of favourable for gelation.

I.6.2.4 Water :

The effect of water concentration is one of the most important parameter in determining the chemical make-up, morphology and size distribution of alkoxide polymers. Unlike the other parameters (e.g. temperature, catalysts, etc.) the water is directly involved in the chemical reactions that form the molecular structure. It must be emphasized, that the role of water concentration goes beyond the chemical requirements of hydrolysis. Yoldas [37] observed the effects of water in silica sol. S. Sakka et al [38] observed that a large water content favours the formation of non-linear on network polymers in the hydrolysis of $\text{Si} [\text{oC H}]_2$. The increase in viscosity of the

solution containning network polymers in the final stage of the reaction is probably due to aggregation of those polymers. It is supposed that this gives the solution an elastic nature, which prohibits the occurence of spinnability. Accordingly the solution becomes the elastic gel without showing any spinnability.

I.6.2.5 Catalysts and pH :

The complete explanation of the effect of catalysts and pH have already been discussed are in section I.8.

I.3. Mechanical Properties :

The gelation time, particle size, agglomeration, miscibility of sets, solid contents of sols, distribution of components are the properties which are affected by mechanical parameters like stirring, ultrasonication and refluxing.

The mechanical parameters, stirring and ultrasonication were used by Hiromichi [39]. Ultrasonication in particular has been used to control the size of the particles framed from alkoxide sols [40]. Zarzycki [41] has attempted to bring in mutual solution mixtures of alkoxide and water without the addition of alcohol as a mutual solvent.

I.7 - Selecting a "Sol-gel" process :

If a "Sol-gel method is to be successfully applied to proceeding of glass [42] and ceramics or to the fabrication of glass and ceramic product, it must be the only method available or it can competitively replace an existing method [43].

Hanning described the uniqueness and advantages of sol-gel process. Briefly, the applications of sol-gel processes are

as follows.

- It involved the use of liquid solution as mixtures of raw materials. Since mixing is with low viscos liquids, homogenization can be achieved at molecular level in a short time.
- The use of synthetic chemicals rather than minerals guarantees high purity.
- Since the reactants are so well mixed in the solutions, they are likely to be equally well mixed at the molecular level when the gel is formed. Thus on heating the gel, chemical reaction will be easy and requires lower temperatures.
- Lower temperature would also suppress phase transformations at higher temp. and thus permit the formation of glasses and ceramics which can't normally be prepared.
- The use of liquid solutions permit the ready fabrication of thin films and fibers [44].
- Impregnation of pores with organic and inorganic materials result in unique composites.
- The modification of structure of metal-organic precursors such that organic groups remain after gelation can yield unique new polymers.
- The "Sol-Gel" process is particularly advantageous for the formation of thin oxide coating [45] for two reasons. For, a dipping route permits the coating of complex shapes relatively

easily. Secondly, very small quantities of raw materials are involved and hence the cost of metal-organic precursors is not a consideration.

- One obvious area which is beyond the scope of this paper is the preparation of ultrafine powders.

- "Sol-Gel" process is ideal for the fabrication of composites by a number of different routes. A filler in the form of fibers or powders can be dispersed in a gelling sol".

I.8 : Drying and sintering of gels :

After gellation, the gels are to be dried and sintered to obtain the glass or ceramic phase. This can be done without cracking of the gel in the case of their fibers and films. However, large gel pieces invariably crack during drying due to the tremendous shrinkage stresses.

Another approach is to powder the dried gel, compact it by dry pressing and then sinter it. Here the major problem is the removal of the trapped hydroxyls and organics. Their evolution may lead to swelling of the sample, porosity or carbon residues. As will be seen, these problems were faced in the present investigation. A major aim of the processing is therefore to minimize the amount of the remaining alkoxy groups. It was with mainly this in view that most of the studies described later have been carried out.

Table 1

Influences of Chemistry related parameters and sol-gel properties.

Parameters	Affected Properties
Precursors :	Kinetics; Structure of digomers; distribution of components
Solvents :	Kinetics : Conformation of precursors; gelation point (solubility of oligomers)
Temperature:	Kinetics; Growth reaction (structure of polymers [crystalline, non-crystalline] solubility (gelation point)
Catalysts :	Kinetics(precursor dependent: in multi-component system different effects on different precursors); distribution of components.
pH :	Catalytic effect of n^{+} and OH^{-} , isoelectric point (gelation) : Kinetics, structure of polymers ; stability of sols
Additives :	Complex formers : Kinetics; solubility; structure and properties of sols; structure of gels; gelation point ; rheology. tensides : surface chemistry of colloids; agglomeration : processing properties of fine particles ; rheology.
Mechanical Parameters :	
Stirring	gelation point; particle size; agglomeration
Ultrasonic treatment	Miscibility; solid content of sols; distribution of components.

CHAPTER - II

SCOPE OF THE PRESENT WORK

In the present work the sol to gel transformation in a sol prepared from titanium tetrabutoxide [TTIB] was studied by measuring the gelation time as a function of acid catalyst and water content. Also the effect of diethanolamine [DEA] on stabilization of sol was studied. Titania sol reacts rapidly with moisture producing a turbid sol. To obtain a clear sol with larger amount of water new techniques like ultrasonication, stirring and refluxing the sol, were developed which stabilize the sol or enhance the life of sol. The gels thus obtained were characterized using thermogravimetry [TG], differential thermal analysis [DTA], X-ray diffraction and scanning electron microscopy [SEM].

In the second set of experiment, powder of lead oxide was mixed in the sol of TTIB. Gelation was carried in a rotary film evaporator. The coated powder thus obtained were calcined to different temperature and the phases obtained were studied using X-ray diffraction, TG and DTA.

CHAPTER III

STUDIES ON SOL-GEL PROCESSING WITH TITANIUM-TETRA-ISOBUTOXIDE SOL

PART - A

III.1 Studies on the processing with Titanium-Tetra-Butoxide Sol

Titanium tetra isobutoxide [TTIB] hydrolyzes rapidly in the presence of atmospheric moisture as indicated by appearance of turbidity. To reduce the rate of hydrolysis and increase the stability of a sol prepared from TTIB, chemicals such as diethanolamine [DEA] are used. For complete hydrolysis, water in the molar ratio 4:1 to TTIB is required. To add this amount of water without destabilizing the sol, considerable quantity of DEA is required which is undesirable. It has been reported that ultrasonication helps to assimilate water in an alkoxide even without the presence of alcohol.

In the present investigation, the effect of DEA, water and ultrasonication on the stability of a TTIB sol are studied. Effect of acid as a catalyst is also investigated. Finally some characterization of the gels studied under different condition has been done by thermogravimetry [TGA], differential thermal analysis [DTA] and X-ray.

As each subsequent experiment dependend to some extent on the result of the previous experiment, the experimental details and results are described together for each experiment.

III.0 CHEMICALS USED:-

Following chemicals were used for all the experiments.

1. Titanium tetra Isobutoxide [TTIB] -

TTIB supplied by "Alfa": It is 99% pure (84% by chemical analysis).

2. Diethanolamine [DEA]

DEA supplied by "BDH" with a minimum assay as 99.00%. It was further distilled in the laboratory to get it more purified.

3. Propanol-2 [Isopropyl alcohol] :

Supplied by "S.D. Fine - Chem Pvt. Ltd. Boisar", A.R. grade

4. Lead II Oxide [Pbo] :

Pbo [Yellow] supplied by "Fluka" with a minimum assay as 99.00%.

5. Hydrochloric Acid [HCl] :

HCl supplied by "Ranbaxy laboratories limited" with a minimum assay 35.4%. It is 12 normal A.R. grade.

6. Glacial Acetic Acid [CH_3COOH] :

Supplied by "Indian drugs and pharmaceuticals Ltd." with a minimum assay as 99.70%. A.R. grade.

7. Acetone [CH_3COCH_3] :

Supplied by "S.D. Fine - Chem. Pvt. Ltd. Boisar" with a

minimum assay as 98.5% A.R. grade.

8. Distilled water [Triple distilled] :

Made in laboratory in a quartz distiller.

EXPERIMENT III.1.1

To determine the time for appearance of turbidity for two different diethanolamine [DEA] contents for different water contents.

III.1.1.2 : Sol composition :

The sol composition is given in Table III.1.1.

III.1.1.3 : Sol preparation :

Take 8 ml of isopropanol and 2.4 ml of TTIB in a beaker. Add measured amount of diethanolamine [DEA] depending on the set. Add another 5 ml of isopropanol to the sol after adding DEA. Then add given amount of water mixed with 3.5 ml of isopropanol to the sol containing TTIB, DEA and isopropanol. Cover the beaker in airtight manner with aluminium foil and cellophane tape. Note the time, when turbidity appears in the sol.

III.1.1.4: Results :

The time of destabilization was noted after adding the amount of water at particular concentration of DEA. Table III.1.1 and Fig. III.1.1 show the time of gellation at different concentration of DEA.

The results show that the sol stability increases with increasing amount of DEA and decreasing quantity of water. Assuming that a processing time of about 1 hr is desirable, Fig. III.1.1 shows in that hour with 0.5 mole of DEA per mole of TTIB, only about 0.7 mol of water can be added which is insufficient for complete hydrolysis.

TABLE III.1.1

Effect of DEA on the amount of water needed to destabilise the sol

	ml	mole	molar ratios
Titanium tetra isobutoxide			
[TTIB]	2.4	7×10^{-3}	1
Isopropanol	16.8	0.2194	31.34
DEA			
Set I	0.2	2.08×10^{-3}	0.30
Set II	0.4	4.16×10^{-3}	0.6

S.No.	Amount of water		Time of gellation	
	ml	$\frac{\text{mole of water}}{\text{mole of TTIB}}$	set I [hr]	set II [hr]
1.	0.5	3.96	-	Imm. turbid
2.	0.4	3.17	Imm. turbidity	0.03
3.	0.3	2.37	0.01	0.05
4.	0.2	1.59	0.07	0.1
5.	0.1	0.79	0.5	1.3
6.	0.09	0.71	0.6	18.05
7.	0.08	0.57	3.25	Can keep for longer time
8.	0.07	0.54	9.47	-
9.	0.06	0.47	Can keep for longer time	-

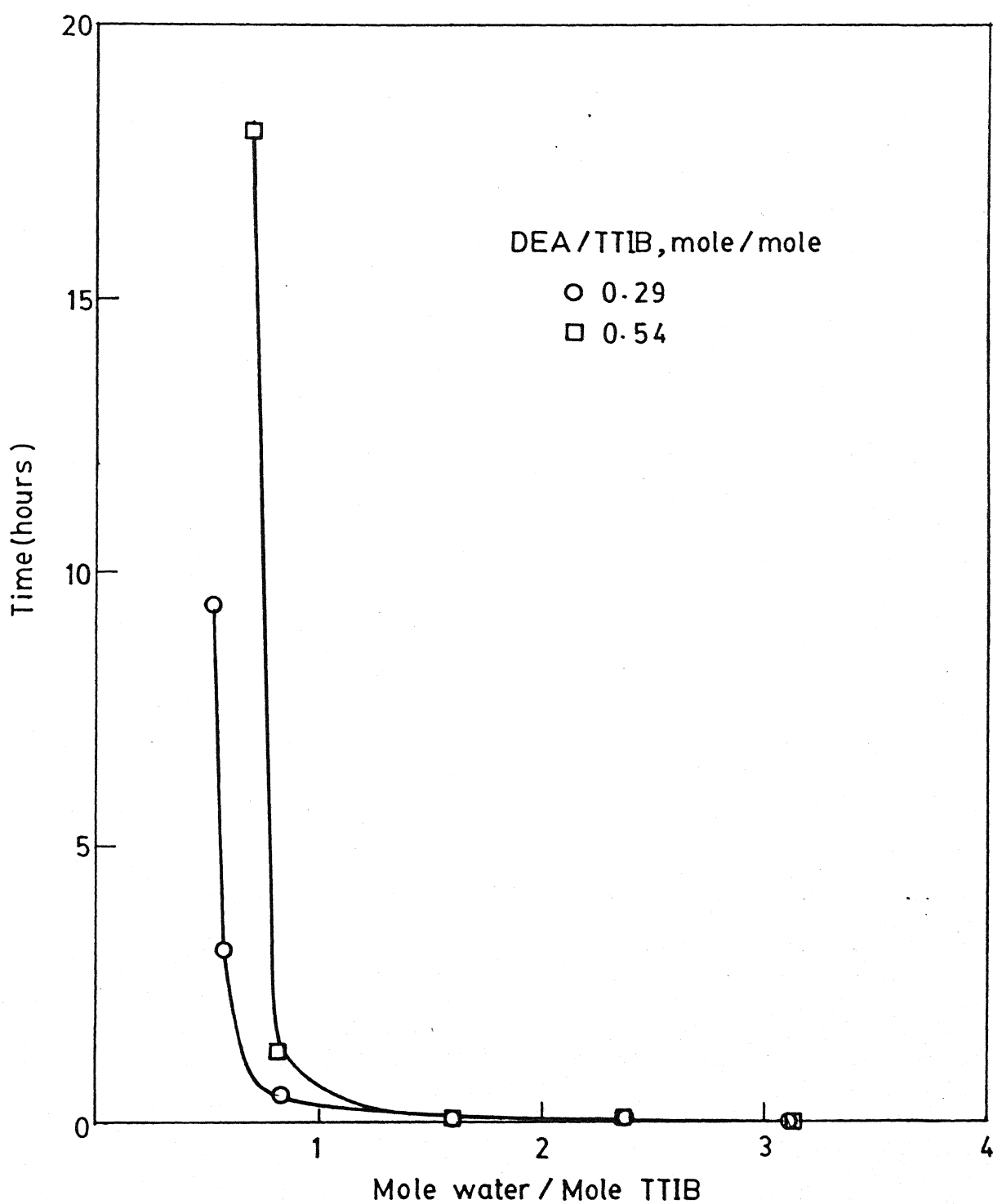


FIGURE NO.

III. 1.1 EFFECT OF DEA on the amount of water needed to destabilise the sol.

EXPERIMENT III.1.2

The effect of ultrasonic agitation on the amount of water needed for destabilization of the sol.

III.1.2.1 Sol Composition : As shown in Table III.1.2.1

III.1.2.2 Procedure :

Initially mix 10 ml of isopropanol and 2.8 ml of titanium tetrabutoxide [TTIB]. Stir for 10 minuts. Add 1.4 ml of DEA and additional 2.8 ml of isopropanol to the sol. Stir for 10 minuts. Then take 0.16 ml of water mixed with 3 ml of isopropanol and pour it in the sol (which is then stirred for 10 minutes after addition of water). Addition of water is followed by ultrasonication using a sonic dismembrator for four minutes. Then add stepwise 0.16 ml of water mixed with 2 ml of isopropanol, followed by ultrasonication for 4 minutes. Repeat it till the turbidity appears in the sol.

III.1.2.3 : Results :

Results are given in Table III.1.2.1. It can be seen that 4 moles of water could be added in the presence of small amount of DEA. The quantity of water could be further increased to 6.5 moles/mole of TTIB if the DEA content was further increased.

TABLE III.2.1

Enhancement of quantity of water by ultrasonic agitation

S. No.	Conc. in	TTIB	DEA	Isopropanol	Amount of water in each step	Total amount of water using ultrasonication
1.	ml	2.8	1.4	15.64	0.16	0.95
	mole	8.2×10^{-3}	1.50×10^{-2}	2.0×10^{-1}	8.0×10^{-3}	5.30×10^{-2}
	molar ratio	1	1.8	25.21	1.09	6.5
2.	ml	15.5	2.6	75.9	0.8	3.2
	mole	0.045	2.7×10^{-2}	9.9×10^{-1}	4.4×10^{-2}	0.17
	molar ratio	1	0.6	22.1	1.00	4.0

EXPERIMENTAL III.1.3 :

Effect of acid catalyst on gelation.

The role of two acids as catalyst was investigated

- 1) HCl
- 2) CH_3COOH

III.1.3.1 : Effect of HCl on gelatation.

III.1.3.1.1 :HCl used is 12 normal.

III.1.3.1.2 :Sol composition :

The overall sol composition is given in the Table

III.1.3.1.1.

III.1.3.1.3 : Sol Preparation :

Take 7.8 ml of TTIB and 15 ml of isopropanol in a beaker. Stir for 10 minutes. Add 1.3 ml of diethanolamine [DEA] and 15 ml of isopropanol to the sol. stir it for at least 3 hours. Beaker should be air tight by using aluminium foil and cellophane tape.

III.1.3.1.4 : Addition of water and HCl :

After stirring for 3 hours, the sol is placed in an ice bath. Add 1.6 ml of water mixed with 9.3 ml of isopropanol using stirring and ultrasonication. Add 0.1 ml of 12 normal

hydrochloric acid [HCl] mixed with 2 ml of isopropanol dropwise using ultrasonication and stirring. The ultrasonication is interrupted particularly so that the sol does not heat up. Turbidity due to formation of particles first appears after some addition of HCl, which then disappears as the sol reprecipitates upon further addition of acid.

III.1.3.1.5 : Results :

The effect of addition of 12 N HCl at 0 °C to the sol is shown in Table III.1.3.1.2.

TABLE : III.1.3.1.1

Sol composition

Conc.	TTIB	DEA	Water	Isopropanol
ml	7.8	1.3	1.6	39.3
Mole	0.0228	0.0135	0.08	0.5133
Molar ratio	1	0.5947	3.5087	22.5140

Effect of addition of 12N HCl at 0

III.1.3.2 : Acetic Acid as Catalyst :

The effect of acetic acid on the time of gellation was determined.

III.1.3.2.1 : Sol composition :

The sol composition is shown in Table III.1.3.3.

III.1.3.2.2 : Sol Preparation :

Take 3.1 ml of TTIB, 8 ml of isopropanol and 0.52 ml of DEA in a beaker. The solution is then stirred for 10 minutes. Then sol is placed in an ice bath to cool down the temperature of the sol to 0° C. Add 0.64 ml of water mixed with 7 ml of

observed increase in the temperature of the endothermic peak.

The exothermic peaks correspond to removal of organics (no crystallization occurs at these temperatures as shown by absence of any X-ray peaks for a sample run upto 350°C). The higher exotherm temperature is reduced quite significantly from 300°C to 280°C as increasing the acid from 0.002 to 0.02.

The TG results also show that the total weight loss decreases as the acid content is increased (Fig.III.1.3.2 and Table III.1.3.6). This shows that the hydrolysis reactions go to greater extent with increasing acid content.

TABLE III.1.3.3

Composition of Sol used to study the effect of the amount of acid

Conc. in	TTIB	DEA	Isosoproponol	Water
ml	3.1	0.52	15.73	0.64
mol	9.0×10^{-3}	5.4×10^{-3}	2.0×10^{-1}	3.5×10^{-1}
molar ratio	1	0.60	22.62	4

isopropanol to the sol dropwise using ultrasonication and stirring. Add different amounts of acetic acid dissolved in remaining isopropanol varying from 0.001 ml to 0.01 ml using ultrasonication and stirring. Then note the time for appearance of turbidity in the sol at 0°C. Results are given in Table III.1.3.3 and III.1.3.4. They are also illustrated through Fig. III.1.3.2. The beaker is then warmed to room temperature to complete the precipitation of particles [is 6 hours]. Keep the beaker in oven at 70°C for 18 hours to get titania gel/powder.

As discussed in the later section, one of the problems faced in conversion of gel to ceramic by heating is that rather large amounts of organics are to be removed. These organics are from the unconverted alkoxy groups. One of the aims of using acid catalyst was to minimize the extent of unconverted alkoxy groups. To study this aspect, thermogravimetric and DTA analysis of the gels were performed.

III.1.3.2.3 : Differential thermal analysis [DTA]:

The DTA ("LINSEIS", model L-62) were carried out on the titania gel, which were heated in air atmosphere upto 1000°C by using a Platinum crucible. The heating rate in DTA runs was 5°C per minute and chart speed was 12 cm per hour. In DTA runs alumina was taken as the reference material. The DTA peaks of pure titania gel containing acetic acid are given in Table

III.1.3.5.

III.1.3.2.4 : Thermal gravimetric analysis [TGA] :

For thermal gravimetric analysis [TGA], the apparatus was set up in the lab by using chemical balance supplied by "Afcoset", a furnace, temperature controller supplied by "Indotherm Instrument Pvt. Ltd. ("Model" Indotherm - 401), variac supplied by ("Automatic Electric Ltd.) and alumina crucible. The heating rate was 10 °C per minute somewhat greater than in DTA runs [5 °C per minute]. The T.G. run of titania gel was carried in air atmosphere from room temperature to 1000 °C. The readings of temperature and weight were recorded at the same time every one minute. The thermogravimetric data is shown in Table III.1.3.6 and Fig.III.1.3.3. .

III.1.3.2.5 : Results :

The DTA shows an endothermic peak and two exothermic peaks. The endothermic peak temperature changes from 111 °C at low acid content to 140 °C at the highest acid content. This peak results due to the removal of absorbed water and hydroxyl groups. The results show that the binding energy of the hydroxyl groups increases with increasing acid content. It is known that in acid catalyzed hydrolysis, the successive hydrolysis of the alkoxy groups on the same molecule becomes more and more difficult as the hydrolysis proceeds. This qualitatively agree with the

TABLE III.1.3.4

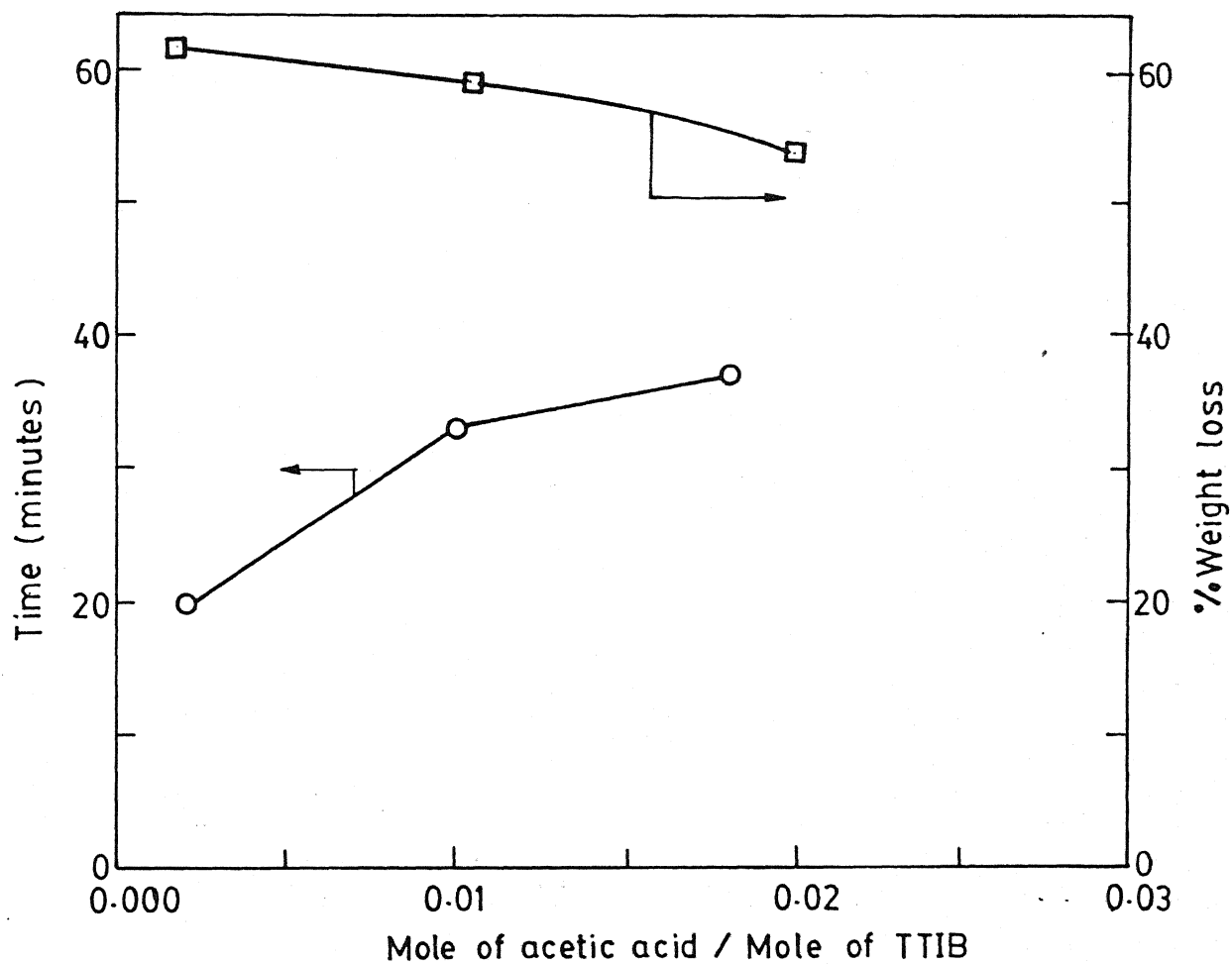
Effect of acetic acid on the stability of composition given in Table III.1.3.3

S. No.	Amount of 17N CH ₃ COOH ml	mole of CH ₃ COOH " " TTIB	Time of gellation (mints.)
I	0.001	0.002	20
II	0.0054	0.010	33
III	0.01	0.020	37

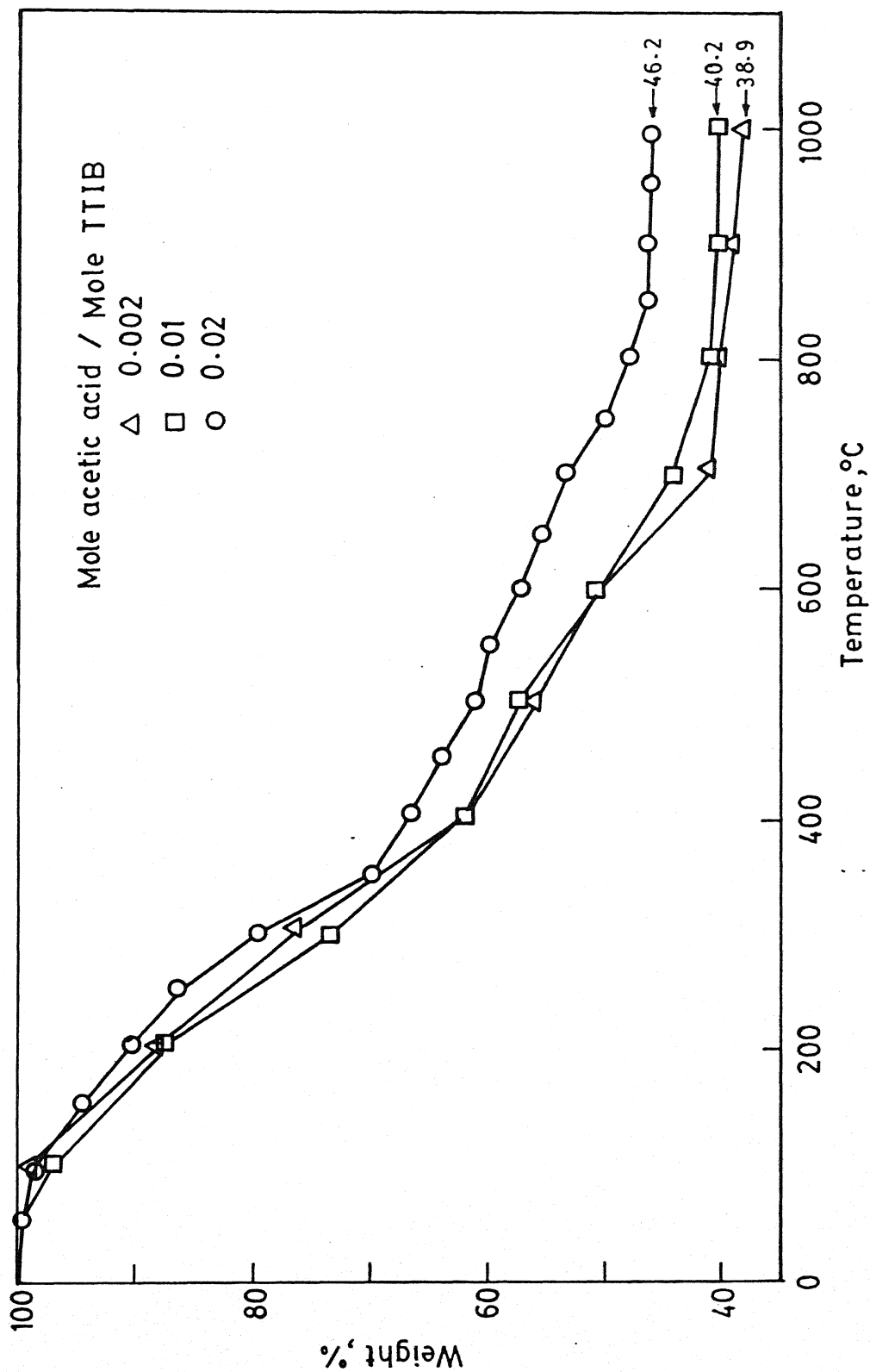
TABLE III.1.3.5

DTA results of the gel made with different amount of acetic acid

S. No.	Amount of 17N CH ₃ COOH ml	mole of CH ₃ COOH " " TTIB	DTA Peaks	
			ENDO[° C]	Exo[° C]
I	0.001	0.002	111	250,300
II	0.0054	0.010	111	250,310
III	0.01	0.020	140	240,280



Fig, No. III. 1.3.1 : Effect of acetic acid on the stability of composition of sol.



Fig, III. 1.3.2. : T.G. Analysis of Titania sol containing different concentration of acetic acid.

TABLE III.1.3

Effect of acetic acid on the wt. loss in percent

S. No.	Amount of CH ₃ COOH ml	Weight loss %
	moles of CH ₃ COOH " " TTIB	
I	0.001	61.1
II	0.0054	59.8
III	0.01	53.8

EXPERIMENT: III.1.4

Effect of the extent of mixing of DEA by refluxing on the amount of water to destabilise the sol is studied.

The resulting titania gel is studied by DTA & TGA.

III.1.4.1 :

Refluxing Apparatus is shown in Fig.III.4.1.

III.1.4.2 : Sol Composition :

Overall sol composition is shown in Table III.1.4.2(a).

III.1.4.3 : Sol preparation :

Take 3.4 ml of TTIB, 15.8 ml of isopropanol and 0.50 ml of diethanolamine [DEA]. Mix all in a beaker. Instead of stirring the sol, reflux it at 90 °C for different times e.g. 1 hr, 2 hrs., 4 hrs. and 8 hrs. Then sol is placed in an ice bath and cooled to 0 °C. At 0 °C, add 0.001 ml acetic acid mixed with isopropanol using stirring and ultrasonication. Then stir the

sol for 30 minutes. Make the water solution with isopropanol [using the ratio of isopropanol to water as 25.6 ml to 2 ml]. Add water dropwise to the sol at 0- 5 °C, stir and ultrasonicate till the turbidity appears.

III.1.4.4:RESULTS:

The results are given in Table III.1.4.2(a). It is seen that there is appreciable increase in the amount of water that can be tolerated and level is on the average higher than without refluxing. After appearance of turbidity the sol is kept in oven at 45 °C for 10 hours; it becomes a solid mass. It is then transferred to another oven at 70 °C for 18 hours. The gel is then characterized by DTA, TGA. Results are shown in Table III.1.4.2(b and c) and Fig. III.1.4.2 to 3.

The DTA of gels after refluxing shows the results similar to that observed earlier Table III.1.4.2(b). The additional peak at 440 to 470 °C may actually have been present in the earlier results, also but not observed due to instrument not functioning in that range at that time. This peak appears to be due removal organics. It was a broad peak in most cases except in the case of 4 hour refluxing where a sharp peak was observed. This need to be confirmed before any conclusion can be drawn.

The results of the Tg analysis of gels prepared with different time of refluxing as given in the Table III.1.4.2(c)

and Fig.III.1.4.3. The steepest rate of weight loss is between 100 to 400 °C. The total weight loss is lower than for similar composition without refluxing Table III.1.3.1.1 showing that hydrolysis reaction is promoted by this rate .the slight increase in weight loss by increasing the time of refluxing to 4 and 8 hrs. appears to be with random variation.

TABLE III.1.4.2(a)

The effect of refluxing on the amount of water needed to destabilize the sol.

		ml	mole	molar ratio
Titanium IV isobutoxid [TTIB]:		3.4	0.01	1
Diethanolamine [DEA]	:	0.6	5.1×10^{-3}	5.1×10^{-1}
Isopropanol	:	16.6	2.2×10^{-1}	21.79
Acetic Acid	:	0.001	1.7×10^{-5}	2.0×10^{-3}

S. No.	Set No.	Refluxing time (hrs.)	ml	WATER mole	molar ratio
1.	I	1	.98	5.4×10^{-2}	5.4
2.	II	2	1.03	5.7×10^{-2}	5.7
3.	III	4	1.09	6.0×10^{-2}	6.03
4.	IV	8	1.18	6.5×10^{-2}	6.5

TABLE III.1.4.2(b)

DTA of titania gel after refluxing effect

Initial temperature	=	35 ^o
Final temperature	=	1000 ^o C
Crucible used	=	Platinum
Heating Rate	=	5 ^o C/minute
Chart speed	=	12 cm/1 hour

S. No.	Refluxing time hours	DTA PEAKS	
		ENDO ^o (C)	EXO ^o (C)
1	1	110	240, 290, 470
2	2	110	240, 290, 470
3	4	110	230, 290, 440
4	8	120	230, 290, 410

TABLE III.1.4.2(c)

Effect of refluxing on the weight loss of the powder

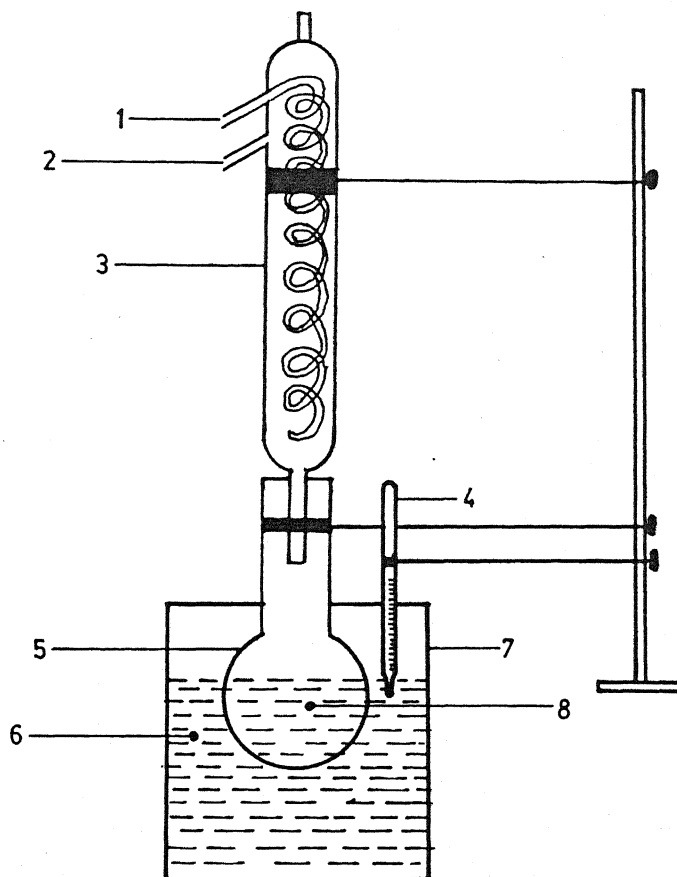
Initial Temperature = 35 °C

Final temperature = 1000 °C

Heating rate = 10 °C/min.

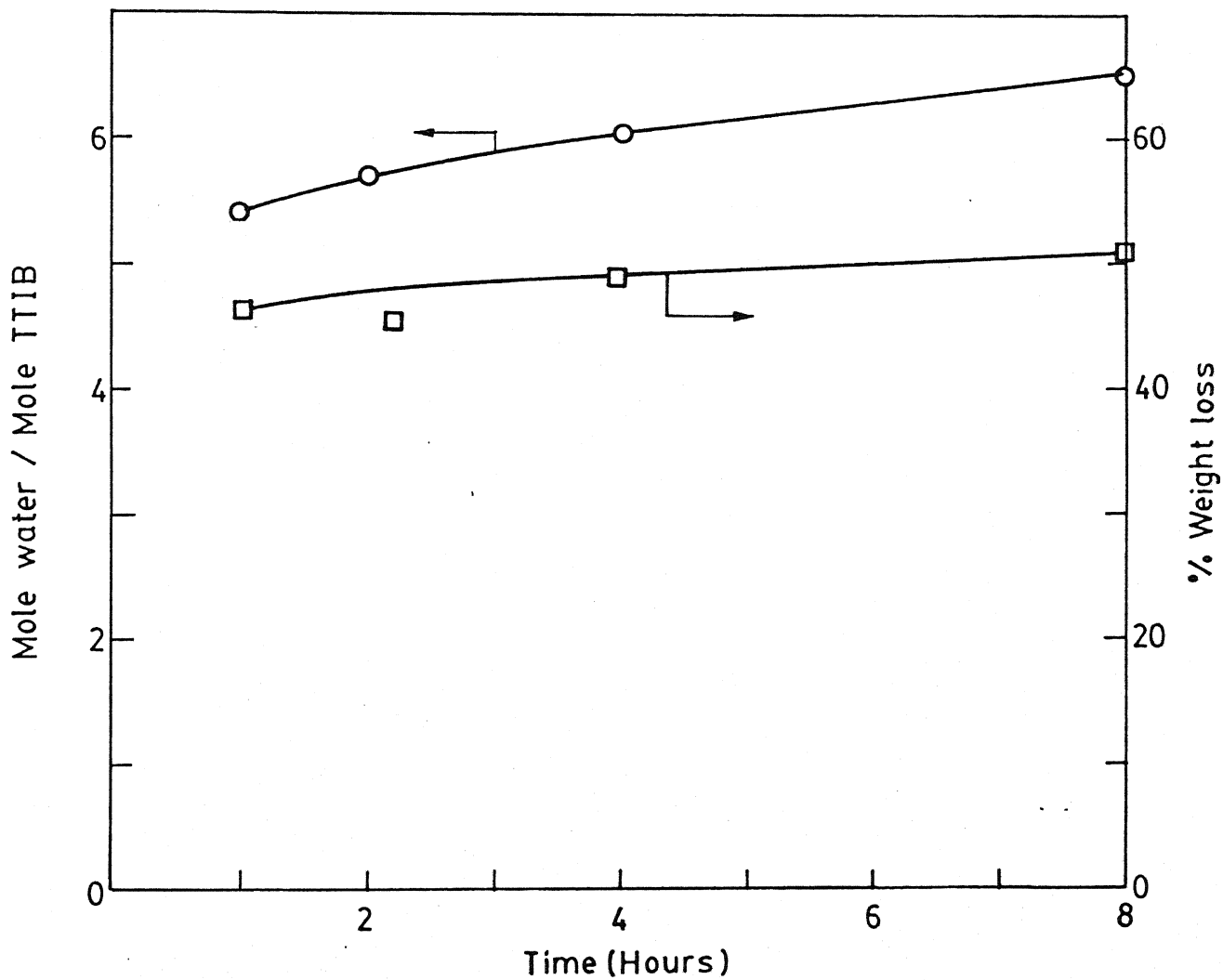
Crucible = Alumina

Sl. NO.	SET NO.	TIME OF REFLUX (Hr.)	% Wt. LOSS
1.	I	1	46.95
2.	II	2	45.49
3.	III	4	48.8
4.	IV	8	50.95

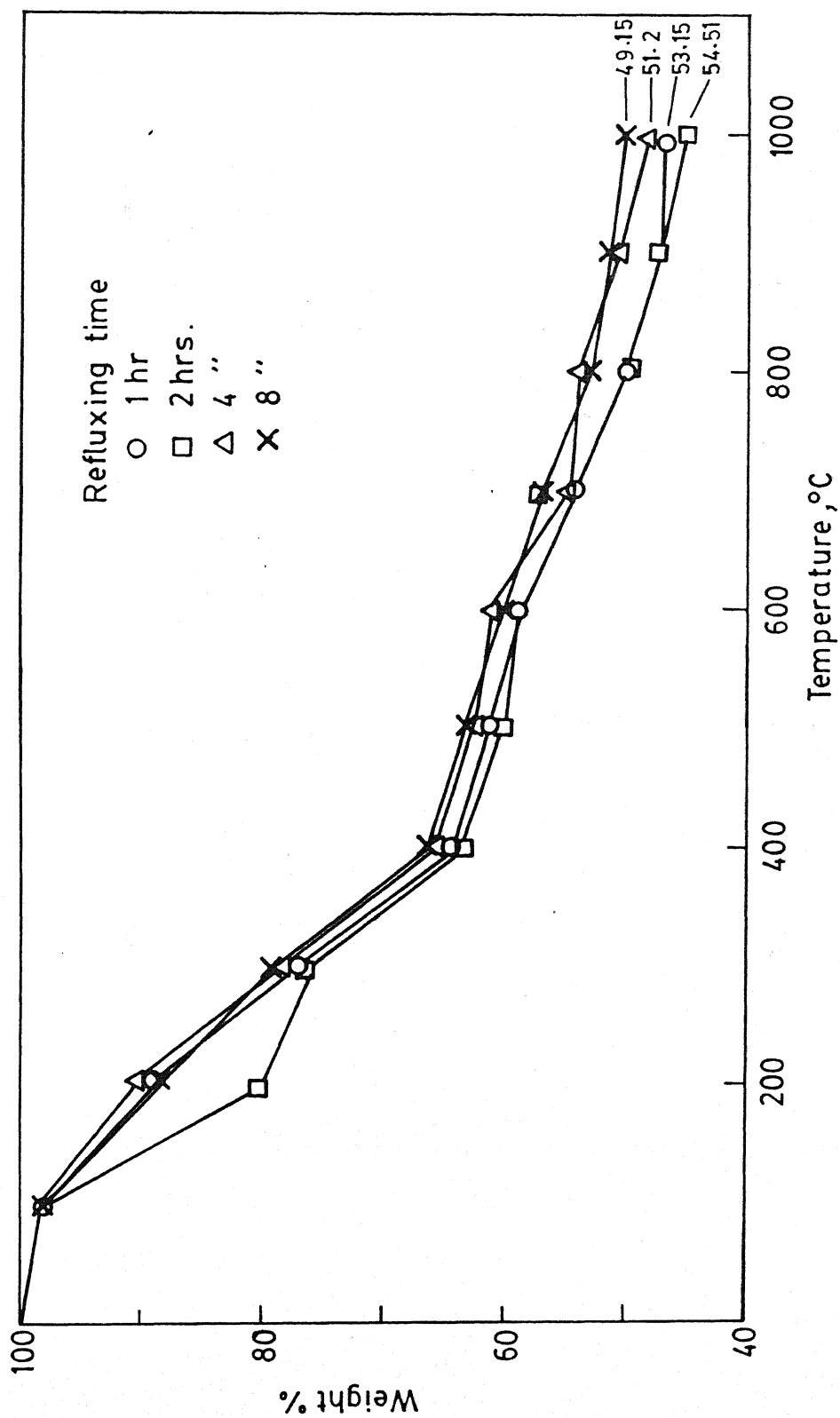


1. Water inlet 2. Water outlet 3. Condensor
 4. Thermometre 5. Round bottom flask
 6. Water 7. Water tank 8. TTIB Sol

Fig, III. 1.4.1. : Refluxing Apparatus



Fig, III. 1.4.2. : Effect of refluxing on the stability of sol.



Fig, III. 1.4.2. : Effect of refluxing on the wt. percent of titania powder.

EXPERIMENT: III.1.5:

Effect of the extent of mixing of DEA on amount of water needed to destabilize the sol and to study the titania gel thus studied by DTA and TGA.

III.1.5.1 : Sol composition :

This is shown in Table II.1.5.1.

III.1.5.2 : Sol. preparation :

Take 3.4 ml of TTIB, 15 ml of isopropanol and 0.58 ml of DEA. Mix all in a beaker. Stir the sol for times of 10 minutes, 30 minutes, 60 minutes and 120 minutes. The rest of the procedure is similar to that followed in section III.1.4.3. The pure titania gel obtained is characterized by differential thermal analysis [DTA] and thermal gravimetric analysis [TGA], results of which given in Table III.1.5.2 and Table III.1.5.3 respectively.

III.1.5.3 Results :

Table III.1.5.1 shows that 6.8 moles of water per mole of TTIB can be added after 2 hours of stirring as compared to 6.5 moles after 8 hours of refluxing. The stirring therefore appears to be much more effective in uniformly dispersing DEA, allowing higher quantity of water to be added.

The DTA and TG results are nearly identical to those obtained for refluxing (Table III.1.4.2(b) and (c)).

TABLE III.1.5.1

Effect of stirring of DEA on amount of water addition

	ml	mole	molar ratio
Titanium tetra Isobutoxide[TTIB]	3.4	.01	1
Diethanolamine [DEA]	5.8×10^{-1}	5.1×10^{-3}	0.51
Isopropanol	16.69	0.2175	21.74
Acetic acid	.001	1.7×10^{-5}	0.002
Water	varied		

S.No.	Set No.	Stirring Time (minute)	ML	WATER (mole)	molar ratio.
1.	I	10	.87	4.7×10^{-2}	4.7
2.	II	30	.92	5.1×10^{-2}	5.1
3.	III	60	1.04	5.8×10^{-2}	5.8
4.	IV	120	1.22	6.8×10^{-2}	6.8

TABLE III.1.5.2
D.T.A. of Titania gel

Initial temperature = 35 °C
 Final temperature = 1000 °C
 Heating rate = 5 °C/1 min.
 Chart speed = 12 cm/1 hr.
 Volt = 0.25 mv.
 Crucible = Platinum

Set No.	Stirring time (min)	DTA PEAKS	
		ENDO (°C)	EXO(°C)
I.	10	120	250,300,480
2.	30	130	250,290,440
3.	60	120	240,300,370
4.	120	120	230,300,410

TABLE III.1.5.3

Thermal Gravimetric Analysis of T. Gel

Initial temperature = 35 °C
Final temperature = 1000 °C
Heating Rate = 10 °C/min.
Crucible = Alumina

S.No.	Set No.	Time of stirring	wt. loss %
1.	I	10 min.	48.5
2.	II	30 "	45.13
3.	III	60 "	47.45
4.	IV	120 "	43.06

Table III 2.1

Sol Composition of titania Coated Lead Oxide

Sample	MLIB ml	moles ratio	DBA ml	moles ratio	VALMP ml	moles ratio	ISOPROP. ml	moles ratio	Ac. ACID ml	moles ratio	Pbo Gm.	P: T molar ratio
PI-I	0.39	0.025	0.2	1.83	0.02	1	49.3	566.3	-	-	10	0.975: 0.025
PI-II	0.39	0.025	0.2	1.83	0.02	1	49.3	566.3	-	-	10	0.975: 0.025
PI-III	0.39	0.025	0.2	1.83	0.02	1	49.3	566.3	-	-	10	0.975: 0.025
PI-IV	1.8	0.1	0.85	1.8	.009	1	47.2	117.3	-	-	10	0.9: : 0.1
PI-V	15.5	1.0	7.6	1.76	1.0	1.23	75.9	22.0	-	-	10	0.5 : 0.5
PI-VI	15.5	1.0	7.6	1.76	1.0	1.23	75.9	22.0	-	-	10	0.5 : 0.5
PI-VII	15.5	1.0	7.6	1.76	1.0	1.23	75.9	22.0	-	-	10	0.5 : 0.5
PI-VIII	15.5	1.0	7.6	1.76	1.0	1.23	75.9	22.0	0.055	0.02	10	0.5 : 0.5

Spin discs used during evaporation = 3 to 8
Dried powder ground by ball mill = 2

Total Sol Volume = 50 ml in 1 to 4
= 100 ml in 5 to 3

PART B

Preparation and characterization of titania gel coated PbO powders

In the preparation of lead oxide based ceramics such as PZT and PLZT, the diffusion and homogeneity of lead is not a problem. It is the nonuniform mixing and low diffusion of the other species such as Zr^{4+} , Ti^{4+} , La^{3+} etc. which results in high sintering temperature, large sintering time and poor homogeneity. Hence it should be beneficial to introduce the latter species by a sol-gel route while the lead can be introduced from PLO powder. In the present work we have studied the problem of coating lead oxide powders with a titania gel. The method basically consists of suspending lead oxide powder in a titanium alkoxide sol and gelling the whole mass together in a rotary evaporator.

III.2.1 : Sample preparation :

A range of Pb : Ti ratio's are used. The compositions were $P_{0.975}T_{0.025}$, $P_{0.9}T_{0.1}$ and $P_{0.5}T_{0.5}$ and are given in the Table III.2.1. The preparation schemes differ slightly depending on the composition and are described below :

Preparation Scheme I :

This scheme was used for preparing samples I to IV in

Table III.2.1. The details for sample I are as follow :

Take 0.39 ml of TTIB and 20 ml of iso-propanol. Stir for 15 minutes. Add 0.20 ml of DEA and additional 20 ml of isopropanol to the sol. Stir for three hours. Take 0.02 ml of water with 9.4 ml of isopropanol. Stir for 15 minutes. The prepared sol is then transfered in a round bottom flask, containing 10 gms. of lead oxide [PbO] powder. Then coat the powder by using rotary evaporator at 60°C. Coated powder is then kept in the oven at 70° C for 6 hours. The dry powder is then scraped out. Thus obtained powder is then ground slowly in mortar and pestle.

Prparation Scheme II :

This scheme was used for sample no. V. In this the sol was prepared as in scheme I but only part of the water [0.8 ml] was added during sol preparation. During rotary evaporation it was noticed that a dry gel did not form and lumpy mass persisted. At this stage 0.1 ml water mixed with 7.4 ml isopropanol each was added twice by interrupting the rotation, thus bringing the total water content to 1 ml. This resulted in a dry gel.

Preparation Scheme III

This scheme was used to increase the water content in the sol without causing turbidity. This was used for samples VI

and VII.

Take 15.5 ml of TTIB and 40 ml of isopropanol. Stir for 10 minutes. Add 7.6 ml of DEA and 15 ml of additional isopropanol to the sol stir for 3 hours. Then take 0.8 ml [1 mole] of water mixed with 5 ml of isopropanol and pore it in the sol. The water addition is followed by ultrasonication using a sonic dismembrater for four minutes. Then add step wise 0.8 ml of water with 5 ml of isopropanol followed again by ultrasonication for 4 minutes. Repeat it for three times so that four moles of water could be added to the sol. Note that the stirring is continuous during addition of water. Pour 10 grams of lead oxide [PbO] powder in the sol. Coat the powder by using rotary evaporator at 60°C with nylon bars added to the mixture to avoid formation of big lumps upon drying.

reparation Scheme IV :

This scheme was used to prepare sols containing acetic acid. Sample VIII was prepared by this method.

Take 15.5 ml of TTIB and 40 ml of isopropanol. Stir for 15 minutes.. Add 7.6 ml of DEA and 15 ml of isopropanol.. After making the sol, seal the beaker air tight by using aluminium foil and cellophane tape. After stirring for 3 hours, the sol is placed in an ice bath. Add 0.8 ml of water mixed with 4 ml of isopropanol. Stir and ultrasonicate it. Repeat the

water addition process for 3 times so that sol contained 3.2 ml [4 mole ratio] of water. Add 0.06 ml of 17 normal acetic acid with 4 ml of isopropanol dropwise using ultrasonication and stirring. Ultrasonication is interrupted periodically so that the sol does not heat up. Coating of PbO is done by using rotary evaporator at 60°C with nylon bars.

Except in samples I and II, nylon bars or teflon coated magnetic spin bars were added to the mixture during rotary evaporation to avoid formation of lumpy mass.

Powder of sample II was ball milled for SEM observation in isopropanol. Other samples are simply ground in a mortar and pestle.

III.2.2 : Heat Treatments :

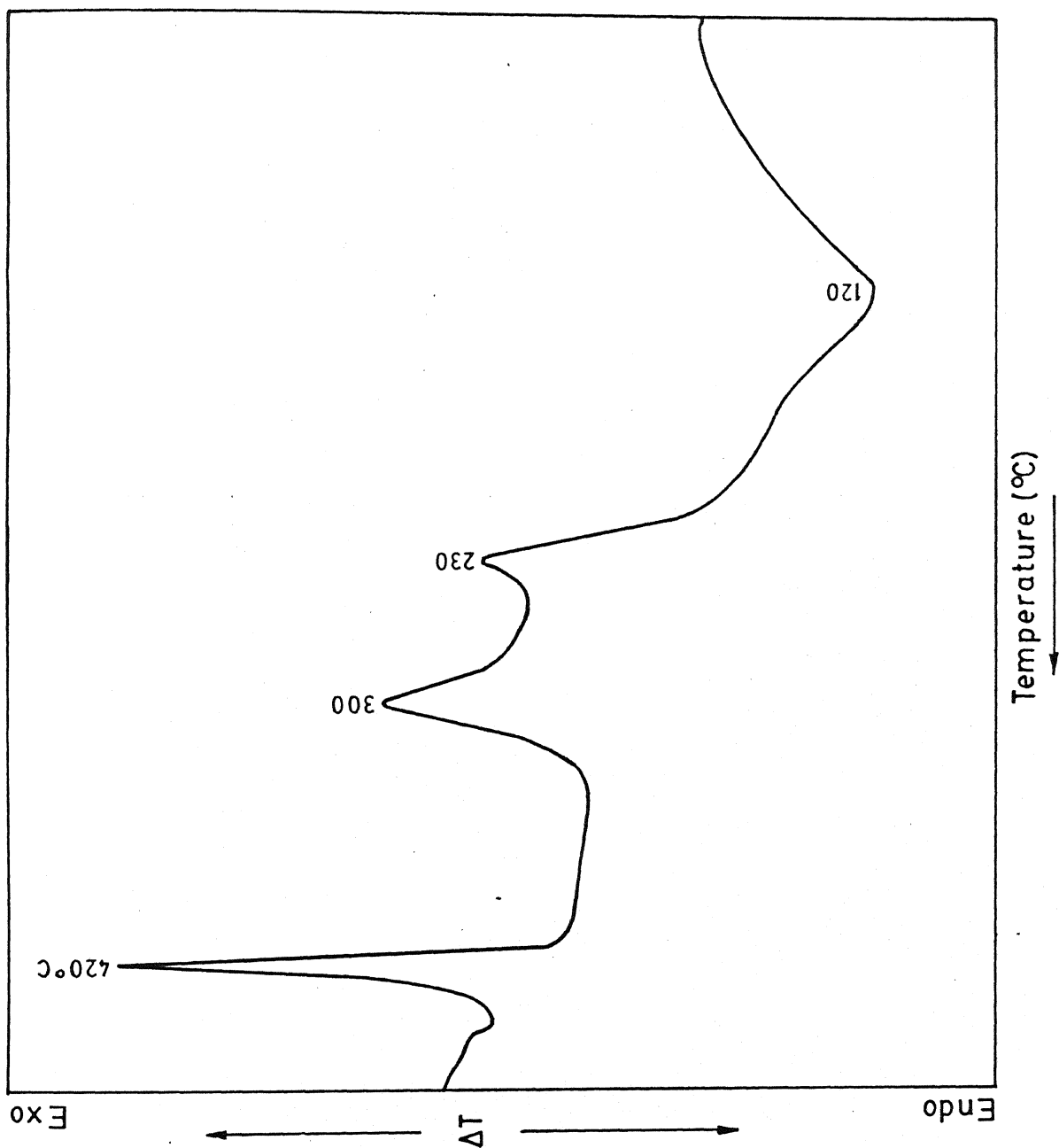
III.2.2(a) Calcination :

Some of the dried and crushed powders are calcined at different temperature e.g. 370°C, 400, 500 and 600°C for different times e.g. : 1, 2 and 4 hrs depending on the sample used as listed in the Table II.2.2. Heat treatments are given in an air atmosphere in a vertical tube furnace. The crucible is covered by "Platinum Lid" to prevent any dust accumulation or impurity deposition from the furnace, during heat treatments. It is found that the powders after calcination had different colours

at different temperatures which are listed in Table III.2.3.

III.2.2(b) Sintering :

After calcination powder is crushed by mortar pestle. Pellets are made by applying the pressure of 8 tons. Then these are sintered at different temperatures e.g.: 700 and 800°C for one hour depending on sample used as shown in Table III.2.3



Fig, No. III. 1.4.3 Differential thermal analysis of titania

Table III.2.2

Heat Treatments of Samples

S.No.	Samples code	Calcination		Sintering	
		Temp(°C)	Time (hr.)	Temp.(°C)	Time (hr.)
1.	P _{0.975} T _{0.025} -I	500	4	700	1
2.	P _{0.975} T _{0.25} -I	500	4	800	1
3.	P _{0.975} T _{0.25} -II	500	4	700	1
4.	P _{0.975} T _{0.25} -II	500	4	700	1
5.	P _{0.975} T _{0.25} -II	600	1	-	-
6.	P _{0.900} T _{0.1} -IV	500	4	-	-
7.	P _{.5} T _{.5} -IV	400	1	-	-
8.	P _{.5} T _{.5} -V	400	1	700	1
9.	P _{.5} T _{.5} -VI	400	2	700	1
10.	P _{.5} T _{.5} -VI	500	2	700	1
11.	P _{.5} T _{.5} -VII	500	1	-	-
12.	P _{.5} T _{.5} -VIII	500	2	800	1

Table III2.3

Powder colour after calcination

S. No.	Calcination temperature (°C)	time (hrs.)	Colour after calcination
1.	350	1	Black
2.	400	1	Dark grey
3.	400	2	Grey
4.	500	1	Large part is grey, small is yellow
5.	500	2	Large part is yellow, small grey
6.	500	4	Yellow
7.	600	1	Radish yellow

III.3. Characterization

III.3.1 Scanning Electron Microscopy of Samples

The pellets obtained after sintering are broken into two or more pieces. The fractured surface were then coated by gold. The conditions of operation are as follows :

The time of coating = 3 minutes

voltage = 3.4 KV

The coating thickness at this time is optimum and sufficient to give good micrographs. Very thick or very thin gold coatings are not to be used. The fracture surfaces were then observed in a JEOL Scanning electron microscope [JEM 840 A, JAPAN]. The micrographs are taken at the magnification ranges from 2000 x to 10,000 x in secondary omission as well as in the back scattered mode. The atomic number of titania is lower than that of lead so the titanium rich sites appear darker in the back scattered mode. The SEM also helps in determining the type of coating e.g. uniform or non uniform.

III : 3.2 : X-ray diffraction

The samples of titania coated lead oxide were treated at different temperatures. The phase analysis for coated powders was then carried out by X-ray diffraction technique using X-ray

diffractometer [Rich Seifert Iso-Debyeflex 20020]. $\text{CuK} [\lambda = 1.5405 \text{ \AA}]$ radiation is used with a monochromator. The powder was ground slowly and spread uniformly over a perspex sample holder. The X-ray diffraction plots [Intensity vs 2θ] of the samples are taken between 25° - 70° in 2θ range.

The parameters used during operation are as follows

- Time constant = 10 secs.
- Current, voltage = 20 mA, 30 KV
- Counts per min. = 1000
- Scanning speed = $3^\circ/\text{min.}$
- Chart speed = 30 mm/min.,

The Bragg's Law is used to calculate the "d" value [Interplanar spacing]

$$n\lambda = 2d \sin \theta$$

where

- n = order of reflection = 1
- λ = wavelength of radiation
- d = Interplanar spacing
- θ = Diffraction angle

III.3.3 : Thermal Analysis [TGA]

Samples of the titania coated PbO after drying and grinding are taken for thermal analysis. The experiments were carried out in air atmosphere. The initial temperature is taken

as room temperature. The final temperatures are given in the Table 3.1. The heating rate was 10°C/min. The T.G. helps in determining the wt. loss of powder with temperature.

III.3.4 : Differential Thermal Analysis [DTA]

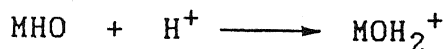
DTA of the titania coated lead oxide [PbO] samples was carried out in air atmosphere using following parameters :

- Initial temperature = Room temperature
- Final temperature = 800°C
- Crucible used = Platinum
- Heating rate = 10°C/min.
- Chart speed = 12 cm/hr.
- Reference powder = Al_2O_3

III.3.5 Electrophoresis :

The Zeta potential of ceramic oxide particles in aqueous suspensions was measured by electrophoresis. The zeta potential of the particle is very sensitive to its surface composition. Thus the existence of a coating or its absence can be determined by measuring the zeta potential of the coated and uncoated particles. Electrophoresis is the migration of electrically charged particles suspended in a colloidal solution

under the influence of an applied electric field. The net charge on the particle surface can be negative or positive depending on the pH



For low pH



For high pH

The pH at which the net charge is zero is called "point of zero charge [ZPC]". A potential is developed on particle due to charge. The potential at a distance at which the particle and adhering liquid layer shears away from the rest of the liquid when the particle moves, can be measured. This is zeta potential which can be measured from the mobility of particles under applied electric field.

$$u = \frac{v}{E}, \quad v = \frac{l}{t}$$

where

v is the velocity of particle under a field $E = \frac{v}{d}$

where, V is voltage across the electrodes

d is the distance between the electrodes.

l is the distance between the grids and t is time

Zeta potential can be measured by using following formula

$$= \frac{3 \eta \mu}{2 \epsilon_0 \epsilon} \quad \text{volts} \quad (1)$$

where

Mobility [μ] = $\text{m}^2 \text{v}^{-1} \text{sec}^{-1}$

Viscosity [η] = $\text{kg m}^{-1} \text{s}^{-1}$

Permittivity of water. [ϵ] = 80.4 at room temp

Viscosity of water [η] = 0.0007 poise .

The titania coated lead oxide powder is calcined at 500°C for two hours. It is then ground slowly for 10 minutes. A very small quantity of the powder is then suspended in 15 ml of 0.01 MKCl solution and the pH of solution adjusted by using nitric acid or NaOH. The particle mobility was measured using electrophorometer [Rank brothers, U.K., Mark II]. Parameters and results are given in Table III. 3.5.1, III.3.5.2 and III.3.5.3

TABLE : III.3.5.2

Measured time for the titania coated PbO particles

S. No.	Particle move to right	pH = 9.98		pH = 4.12	
		Time (secs.) Particle moves to left		Time R.H.S.	L.H.S.
1.	6.34	7.36		11.73	13.07
2.	6.63	6.94		12.5	21/17
3.	5.98	6.44		13.7	14.62
4.	7.35	7.33		12.28	13.74
5.	6.24	5.91		12.01	14.09
6.	6.67	6.99		11.89	13.62
7.	6.35	7.21		12.29	13.55
8.	6.99	7.51		13.72	13.87
9.	7.00	6.99		12.51	13.91
10.	6.35	7.02		13.29	14.28

Table : III.3.5.3

Table for Results

S.No.	Parameters	pH = 4.12	pH =
1.	Mean time	13.65	6.84
2.	Mobility [m ² Volt ⁻¹ sec ⁻¹]	0.12×10 ⁻⁷	0.23×10 ⁻⁷
3.	Zeta potential	+16.8	-42.16

CHAPTER-IV

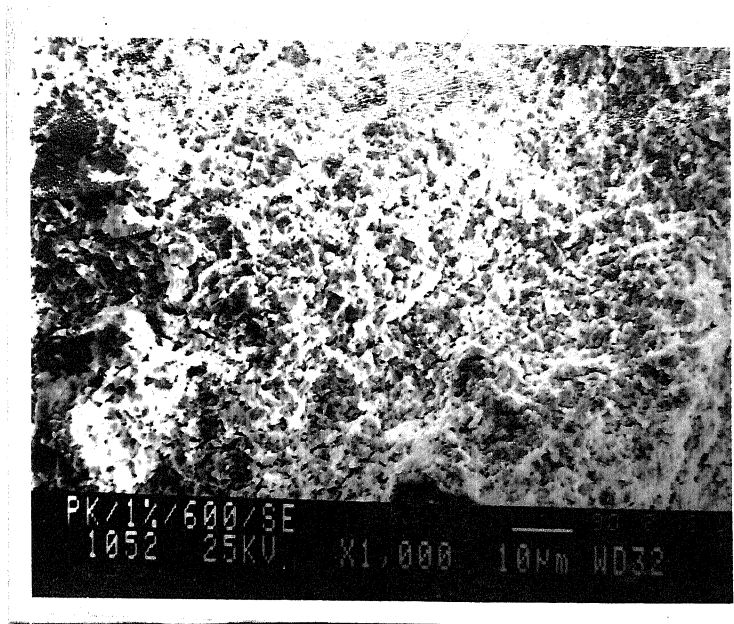
RESULTS AND DISCUSSION

IV.1. Scanning electron microscopy [SEM] :

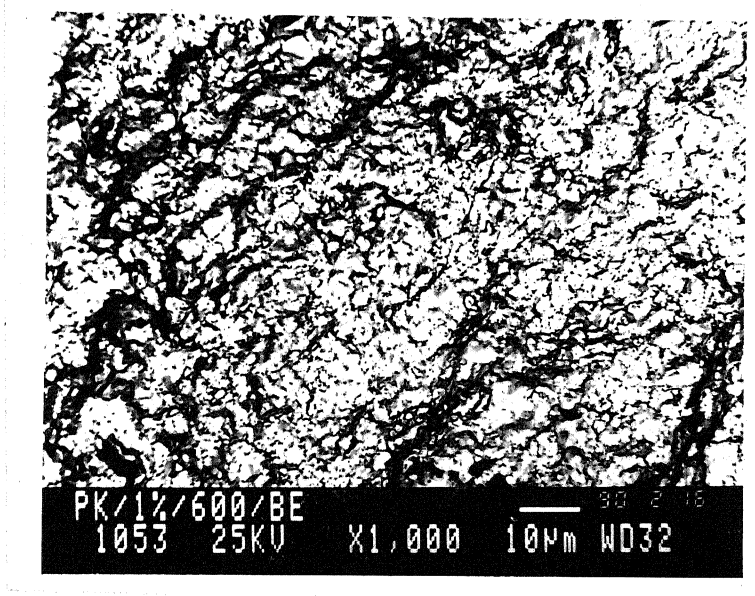
The titania coated lead oxide was calcined and made into pellets. Some of the pellets were sintered. Fracture surfaces of the calcined powder compacts and the sintered pellets were examined in SEM in the secondary emission as well as in the back scattered mode. The atomic number of titanium is smaller than lead so the titania rich region appears darker in back scattered image.

Fig. IV.1(a,b), IV.2 are the micrographs of the fracture surface of calcined pellets. Titania is clearly visible as dark are scattered around the grain as well as inside the grain in the back scattered mode. But there is some portion in which titania distribution is denser. This shows that the coating around the particles is not very uniform and there are regions of titania in chunks.

Fig. IV.3.(a.1) are the micrographs of fracture surface of sintered pellet. The smaller titania spots have disappeared. Very small or no titania remains inside the grains. In sintering temperature is higher than calcination so titania may have diffused in from the surface of grains to the bulk.



(a)



(b)

Fig, No. IV. 1. (a): Scanning Electron micrographs of calcined
and (b) Titania coated lead oxide.

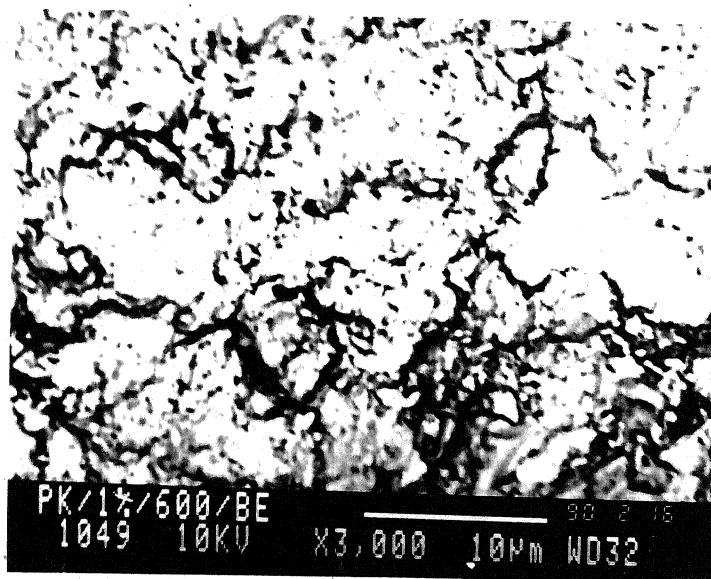
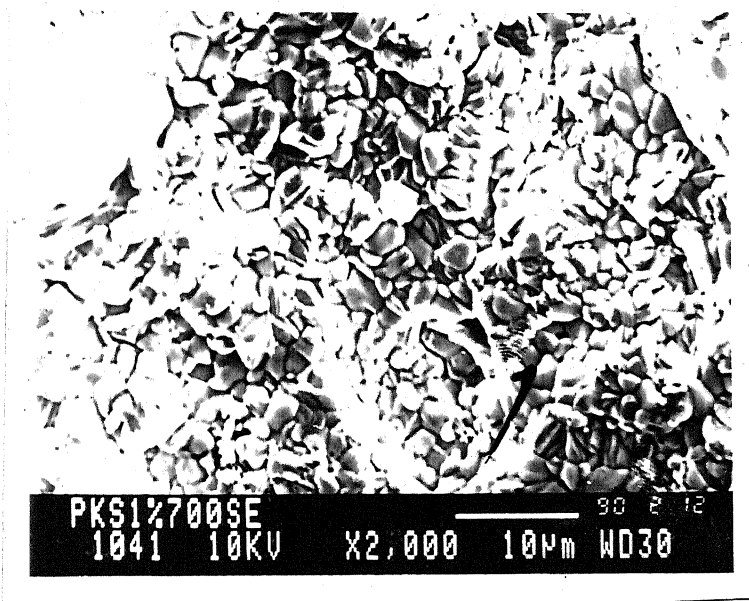
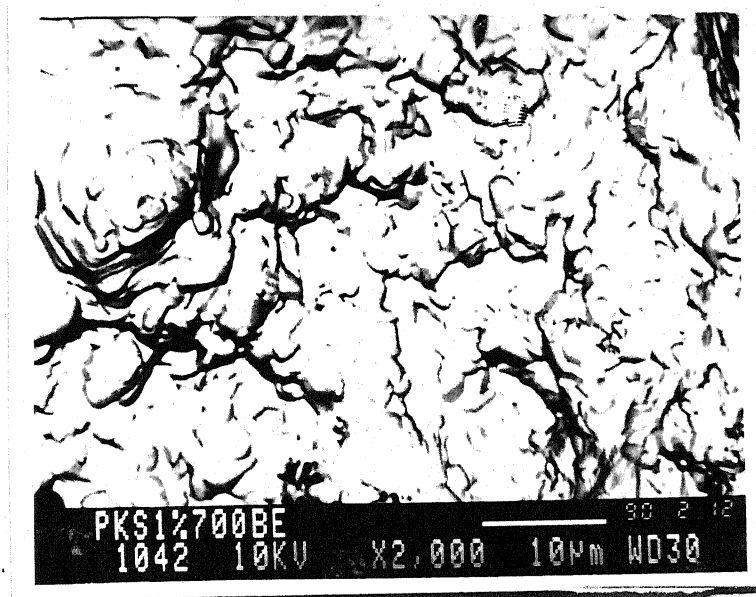


Fig. IV. 2.: (a) : Scanning Electron ~~micrograph~~ micrograph of calcined Titania coated lead oxide.



(a)



(b)

Fig, No. IV.3 (a) and(b): Scanning Electron micrographs of sintered Titania coated lead oxide.

IV.2 Thermogravimetric analysis [TGA].

The samples were heated at 10°C/hr. and their weight with time was recorded. The wt. loss can be calculated as follows :

In the sample,

Amount of PbO taken = a gm

Amount of TTIB taken = v ml

wt. of gel + PbO before TG = x gm.

wt. of $\text{PbO} + \text{TiO}_2$ after TG = y gm

It was determined that 1 ml of TTIB has 0.1871 gm (p) of TiO_2 .

Therefore initial amount of TiO_2 in TTIB = v x p gms.

After TG, amount of PbO (q) = $y \times \frac{a}{a + vp}$

Therefore % weight loss = $\frac{x-y}{x-q} \times 100$

The results are shown in Table IV.1.1 which shows that the weight loss is very much affected by amount of water and use of catalyst. If the mole for mole of water per mole of alkoxide are increased from 1.25 to 6 then weight loss decreases from 73.26% to 55.1% upto 600° . It is due to higher water content which may increases the hydrolysis. The hydrolysis causes more alkoxide groups to be replaced by OH. It leads the decrease in weight loss.

Similarly addition of catalyst e.g. acetic acid may enhance the hydrolysis and leads to decrease in the weight loss as shown in table IV.1.1 Increasing the acetic acid concentration from 0 to 0.02 mole per mole of TTIB reduces the weight loss from 73.85% to 55.1%.

IV₃ X-Ray analysis :

The pellets after heat treatments as shown in Table IV.2.2 were examined by X-ray. The calculated 'd' value and the corresponding intensities are compared with standard data. The ASTM data for PbTiO_3 and PbO are shown in table IV3.1 & IV3.2 respectively. The X-ray analysis of different samples are given in Table IV 3.3 to 3.8.

The results of X-ray analysis of the samples after various calcination and sintering treatments are summarised in Table IV.3.9. All the samples show lead titanate and PbO phases. This shows that the formation of lead titanate in coated powders can occur at 400°C , much lower than 580°C for the mixed oxide case. The presence of PbO in all the samples led to the possibility that the TTIB used may not be 100% pure. It was analyzed by preparing a gel and calcining the gel to 1000°C . The yield was only about 84% of that expected. The TTIB is then a solution of the compound in some alcohol, which is usually the case. This resulted in all samples being deficient in titania

from the 50:50 composition. The analysis of the strength of the peaks shows that sintering at 800°C is needed to complete the reaction.

Table IV.1.1

T.G. OF TITANIA COATED PbO SAMPLES

S. No.	Sample Code	Final Temp. (°C)	Holding time (Hr.)	Initial weight (x)	Final weight (y)	weight loss %
1.	PT-V	600	1	1.0749	0.649	73.26
2.	PT-VI	600	1	0.4753	0.2908	73.85
3.	PT-VII	600	1	1.1179	0.8761	55.10
4.	PT-VIII	600	1	0.7498	0.5677	58.79

TABLE IV.3.1

ASTM DATA FOR LEAD TITINATE [PbTiO₃] [TETRAGONAL SYSTEM]Radiation used CuK α

Wave length (= 1.5405

File no. = 6.0452

S. No.	d(A)	I/I ₀	hkl	2 θ
1.	4.15	25	001	21.41
2.	3.90	50	100	22.91
3.	2.84	100	101	31.50
4.	2.75	55	110	32.50
5.	2.29	40	111	39.48
6.	2.07	16	002	43.73
7.	1.95	30	200	46.57
8.	1.83	14	102	49.83
9.	1.76	10	201	51.96
10.	1.74	12	210	52.61
11.	1.65	20	112	55.70
12.	1.60	40	211	57.61
13.	1.42	14	202	62.78
14.	1.38	04	003	67.92
15.	1.37	10	220	68.48

TABLE IV.3.2
ASTM DATA FOR LEAD OXIDE [PbO]

Radiation Cuka

Wavelength = 1.5405

File No. 5 - 0570

S. No.	d(A)	I/I ₀	hKl	2θ
1.	5.89	6	001	15.03
2.	3.06	100	111	29.12
3.	2.95	31	002	30.34
4.	2.74	28	200	32.63
5.	2.49	<1	201	36.04
6.	2.38	<1	020	37.85
7.	2.203	12	112	39.56
8.	2.013	2	211	40.96
9.	1.85	14	212,022	45.15
10.	1.79	14	220	46.25
11.	1.73	15	113	49.25
12.	1.64	13	311	50.80
13.	1.59	<1	203	53.12
14.	1.53	9	222	56.08
15.	1.51	2	213	57.76

TABLE : IV.3.3

X-RAY DATA FOR PbO COATED WITH TiO₂ CALCINED AT 400 °C FOR 1 HrPT-V_a

Y Peak no.	2θ (degrees)	d (Å)	I/I ₀	Phases	hKl
1.	28.78	3.067	100	PbO	E111
2.	32.01	2.758	55	PT	110
3.	52.52	1.744	12	PT	210

TABLE ; IV 3.4

X-RAY DATA FOR PbO COATED WITH TiO₂ CALINED AT 400°C FOR 1 HOUR
AND SINTERED AT 700°C FOR 1 HOUR

Sample : PT-V

Peak no.	2θ degrees	d (Å)	I/I ₀	Phases	hKl
1.	31.51	2.842	100	PT	101
2.	39.52	2.278	<1	PbO	112
3.	46.52	1.95-	30	PT	200
4.	57.73	1.596	<1	PbO	203

TABLE ; IV.3.5

X-RAY DATA FOR PbO COATED WITH TiO₂ CALCINED AT 400 C FOR 2 HRS.
AND SINTERED AT 700°C FOR 1 HOUR

Sample : PT-VI_a

Peak no.	2 θ degrees	d (Å)	I/I ₀	Phases	hkl
1.	21.41	4.15	25	PT	001
2.	22.98	3.90	50	PT	111
3.	29.11	3.06	100	PbO	111
4.	31.50	2.84	100	PT	101
5.	32.52	2.75	55	PT	110
6.	36.02	2.49	≤ 1	PbO	201
7.	39.56	2.27	< 1	PbO	112
8.	43.72	2.08	16	PT	002
9.	52.59	1.74	12	PT	210
10.	55.71	1.61	40	PT	211
11.	57.76	1.59	< 1	PbO	203

TABLE IV.3.6

X-RAY DATA FOR PbO COATED WITH TiO₂ CALCINED AT 500⁰C FOR 2 HOURS
AND SINTERED AT 700⁰ FOR 1 HOUR

Sample : PT-VI_b

Peak no.	2θ degrees	d (Å)	I/I ₀	Phases	hkl
1.	21.41	4.15	25	PT	001
2.	29.11	3.06	100	PbO	111
3.	31.52	2.84	100	PT	101
4.	32.58	2.75	55	PT	110
5.	39.60	2.27	<1	PbO	112
6.	46.75	1.95	30	PT	200
7.	52.55	1.74	12	PT	210
8.	55.65	1.61	40	PT	211
9.	57.76	1.59	<1	PbO	203

TABLE IV. 3.7

X-RAY DATA FOR PbO COATED WITH TiO₂ CALCINED AT 500°C FOR 1 HR.

Sample PT-VI

Peak no.	2 degrees	d (Å)	I/I ₀	Phases	hkl
1.	22.88	3.90	50	PT	100
2.	28.75	3.06	100	PbO	111
3.	31.50	2.84	101	PT	110
4.	39.56	2.203	12	PbO	112
5.	46.57	1.95	30	PT	200
6.	57.76	1.59	<1	PbO	203

TABLE IV 3.8

X-RAY DATA FOR PbO COATED WITH TiO₂ CALCINED AT 500°C FOR ONE HOUR AND SINTERED AT 800°C FOR 2 HRS.

Sample-PT-VIII

Peak no.	2 θ degrees	d (Å)	I/I ₀	Phases	hkl
1.	21.41	4.15	25	PT	001
2.	29.11	3.06	100	PbO	111
3.	31.56	2.84	100	PT	101
4.	32.50	2.75	55	PT	110
5.	36.02	2.49	21	PbO	201
6.	39.84	2.20	12	PbO	112
7.	46.54	1.95	30	PT	200
8.	55.70	1.65	20	PT	112
9.	57.43	1.51	2	PbO	213

TABLE :IV.3.9
PHASE ANALYSIS OF TITANIA COATED PbO SAMPLES

S. No.	Sample code	Treatments				Phases detected
		Calcination °C	Hrs.	Sintering °C	Hrs.	
1.	PT-V _a	400	1	-	-	PbO,PT
2.	PT-V _b	400	1	700	1	PbO,PT
3.	PT-VI _a	400	2	700	2	PbO,PT
4.	PT-VI _b	500	2	700	1	PbO,PT
5.	PT-VII	500	1	-	-	PbO,PT
6.	PT-VIII	500	1	800	2	PbO,PT

IV.4 : Differential thermal analysis [DTA]

The DTA peaks of titania coated lead oxide reveal the temperature of the dehydration of water removal of organics and formation of lead titanates.

DTA could be carried out only on two samples due to malfunctioning of the instrument. The primary aim was to see if there is any lowering in the temperature at which lead titanate forms. Exothermic peaks were found at 120°C , 190° , 370° and 460° . The last peak corresponds to the formation of lead titanate. The corresponding peak in the mixed oxide samples is reported at 590°C []. Thus the temperature for the formation of lead titanate from PbO and titania gel is lowered by more than 130°C .

CHAPTER V

CONCLUSIONS

The aim of the experiments conducted on processing with titania sol were to find condition for increasing the stability of sol and also for reducing the weight loss on calcination. The former is needed to provide enough time for precesses and the latter for ensuring a minimum of unhydrolysed alkoxy groups. Following conclusion emerged.

1. Addition of DEA incrases the stability of sol. Experiments indicate that about 0.6 moles DEA per mole of TTIB are needed to stabilize the sol for sufficient time for processing.
2. Increased amounts of water decrease the sol stability. With about 0.6 mole/mole DEA, only 1 to 2 moles of water can be added to yield a sol life of only a few minutes.
3. The stability of the sol can be further increased by small additions (0.002 mole/mole) of acetic acid.
4. The amount of water can be increased if the water additions are done in small steps with ultrasonic agitation in between the addition. It was possible to increase the water content to about 4 moles/mole by this method without distabilizing the sol.
5. A further dramatic increase in the amount of water that can be tolerated to 6.5 moles/mole occurs if the mixture of TTIB + DEA + isopropanol is refluxed or stirred for extended time. This

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